

Applications of Allophane in Mortars and Asphalts: Predictive Modeling and Improvement of Physical-Mechanical Properties

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Abstract

Allophane, a nanoporous micromaterial of volcanic origin, can improve impermeability, strength, and durability. In an initial stage involving mortars, allophane was characterized using SEM and TEM microscopy, which revealed its amorphous nature. An optimization model based on cubic splines implemented in Python was developed and applied to mortar mixtures (prepared according to ASTM C270 and NTE INEN 2518 standards), which allowed the identification of allophane dosages capable of reducing water absorption by up to 23.7% compared to the standard (0.5% additive in ratio cement to sand 1:5, after 28 days of curing). The waterproofing tests were conducted in accordance with ASTM C1585. The model also predicted an optimal dosage of 0.41%, demonstrating the usefulness of integrating predictive modeling with experimental validation. In a second stage, concerning asphalts, the impact of allophane on asphalt mixtures was evaluated using a conventional design mix with 95.1% crushed stone aggregates and 4.65% AC-20 asphalt, modified with 0.25% of allophane. The mixtures were characterized by indirect traction tests—rigidity modulus at different temperatures (10°C, 20°C, and 40°C), aging in accordance with AASHTO R-30 standards, as well as Marshall stability and flow tests, volumetric properties, Cantabro wear, FTIR, and TGA. The results show that allophane increases the strength and extends the service life of asphalt mixtures by $28.92 \pm 2\%$ compared to conventional mixtures, improving adhesion, cohesion, and compatibility. Overall, these findings con-

firm allophane as a versatile and promising nano-additive for optimizing mortars and asphalts, providing sustainable and high-performance solutions in the construction industry.

Keywords

Allophane, Aging, Asphalt Mixtures, Resistance, Durability, Nano-Additive, Mortar Waterproofing, Optimization Model

1. Introduction

Allophane is a versatile nano-additive with potential applications in various construction materials. In this study, it is examined in two specific areas: 1) mortars, where its effect on waterproofing and dosage optimization is analyzed, and 2) asphalt mixtures, where its impact on pavement strength and aging is evaluated. For this reason, two parallel and independent lines of research are being developed, each dedicated to contextualizing and assessing the contribution of this material in its respective field.

The ongoing demand for more durable and resistant construction materials has driven research into the incorporation of nanomaterials capable of improving performance in aggressive environmental and mechanical conditions. In this context, volcanic nanoclays have become promising additives due to their high specific surface area, chemical reactivity, and ability to interact with binding matrices at the micro and nanoscale. This study is based on the general hypothesis that the unique nanostructured morphology of allophane can improve the durability of construction materials by modifying the microstructure of their binding matrices, both in cementitious and bituminous systems. Although the interaction mechanisms differ, with physicochemical interactions with hydration products in cement-based materials and physicochemical interactions with polar fractions of the asphalt binder in bituminous mixtures, the expected effect converges on a common improvement in resistance to degradation, aging, and moisture-induced damage processes. Within this framework, the research is structured around two parallel but complementary studies: 1) the evaluation of allophane as a nanotechnological additive in cement mortars to reduce water absorption and improve durability, and 2) the evaluation of asphalt mixtures modified with allophane to improve mechanical performance and resistance to aging. Together, these studies aim to provide a unified perspective on the potential of allophane as a multifunctional nanomaterial for infrastructure applications.

1.1. Mortar Analysis

First, in civil engineering projects, it is common to encounter various problems that manifest as surface imperfections. These defects arise from changes concrete undergoes due to external factors [1]. The most common defects are reinforce-

ment corrosion and crack formation, which compromise the long-term stability of structures. Mortar is a fundamental material in the construction of walls and masonry elements due to its reliable performance as a coating and its bonding capacity. However, moisture is a critical factor that can significantly alter its properties. This limitation can be either mitigated or reduced by using construction additives.

A wide variety of additives are available on the market that are incorporated during mixing to improve the material's properties. These contribute to reducing execution times, increasing project efficiency, and modifying key properties such as workability, strength, and setting and hardening times [2].

Previous investigations have demonstrated the versatility of allophane due to its surface area and porosity. This amorphous aluminum silicate mineraloid, having the idealized formula $\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{1.3-2} \cdot (2.5-3) \cdot \text{H}_2\text{O}$, has applications in various industries [3]. In masonry mixtures, it has been used primarily as an additive to improve compressive strength in cement grouts for oil wells and in hydraulic cement concretes, resulting in a 9.4% increase in strength [4].

This study is a part of the results of the preliminary research titled "ALLOPHANE AS A NANOTECHNOLOGICAL ADDITIVE IN MASONRY MATERIALS TO INCREASE RESISTANCE AND WATERPROOFING" which details the methodology used. In this paper, the essays used to obtain absorption percentages are briefly described.

The allophane was sieved using mesh sizes No. 40, 140, and 325 and activated at 180°C. For mortar mix cubes, samples were prepared with cement-to-sand ratios of 1:3, 1:4, and 1:5, and allophane concentrations of 0%, 0.5%, 1%, 1.5%, and 2%, along with an additional 1.5% cement mix for comparison. Preparation followed ASTM C270 [5] and NTE INEN 2518 [6] standards, while waterproofing tests were performed according to ASTM C1585 [7]. The water absorption percentage was evaluated at the 7th and 28th days of curing to identify the optimal combination for capillary absorption and to assess allophane's performance as a waterproofing material.

Mortar dosing is a complex process due to the need to balance variables such as the cement-to-sand ratio, water content, and additive incorporation, all of which directly affect properties such as strength, workability, and absorption. This complexity makes decision-making difficult, as slight variations can significantly impact the material's performance. In this regard, an optimization model is an effective tool for simultaneously analyzing multiple factors and predicting optimal combinations.

1.2. Asphalt Analysis

Research on asphalt pavements, driven by the need to improve the durability of road infrastructure, faces persistent challenges that compromise the longevity and efficiency of roads, leading to cracking, deformation, and oxidation, driven by the combination of mechanical factors (*i.e.*, repetitive traffic loads), environmental

factors (*i.e.*, thermal and climatic changes), and chemical factors (*i.e.*, asphalt binder degradation).

The road infrastructure sector, in its ongoing search for innovative materials to enhance the physical and mechanical properties of asphalt mixtures, considers nanomaterials as a promising additive. Thanks to their properties, these materials are attracting attention in pavement engineering. Among them is allophane, a volcanic nano-clay that has shown promising results in previous research [8].

The dosage and optimal design for the preparation of asphalt mixtures was taken as a reference from previous research, where the master formula obtained consists of 95.1% stone aggregates (*i.e.*, 25% coarse aggregate $\frac{3}{4}$ ", 25% medium aggregate $\frac{1}{2}$ ", and 50% of fine aggregate-sand) and 4.9% AC-20 asphalt for conventional mixtures; as well as 95.1% stone aggregates, 4.65% AC-20 asphalt with 0.25% allophane for modified mixtures [9].

The research project aims to evaluate the contribution of the nanomaterial allophane as an additive that extends the service life of flexible pavements (*i.e.*, asphalt mixtures) and reduces associated maintenance costs [10]. The study focuses on the use of allophane as an additive in asphalt mixtures and on its impact on pavement properties. It seeks to explore the application of allophane as an additive in asphalt mixtures with potential for industrial commercialization, in accordance with the General Specifications for the Construction of Roads and Bridges MOP-001-F 2002 and corresponding international standards. [11].

This study builds upon the results obtained in the preliminary research entitled "Analysis of the resistance and aging of asphalt mixtures modified with allophane through the characterization of physical-mechanical and rheological properties," which arises from the need to evaluate the potential of allophane as a sustainable additive to optimize the resistance and increase the aging performance of asphalt mixtures—establishing a comparison between conventional and modified mixtures to evaluate their behavior under different temperature and aging conditions [12].

2. Methodology

2.1. Mortar Analysis

2.1.1. Characterization of the Additive by Microscopy

Prior to characterization, the allophane used in this study was obtained from volcanic ash-derived soils (Andisols) located in the province of Santo Domingo de los Tsáchilas, Ecuador, where this mineraloid commonly forms through the weathering of recent volcanic deposits (Ecuadorian case 4 meters). This geological origin is associated with a high content of amorphous aluminosilicates, which makes the material particularly suitable for surface modification and use as a functional additive.

Subsequently, the allophane was thermally activated at 180°C to moderately modify its surface and improve its performance as an additive without affecting its amorphous structure. This approach is based on previous studies indicating

that adsorbed water is removed around 100°C, while partial loss of hydroxyl groups (dehydroxylation) begins at 150°C [13]. It has also been reported that significant surface changes occur between 150°C and 250°C without compromising the material's texture or porosity [14]. Therefore, the choice of a temperature of 180°C for the activation of the allophane induces surface chemical modifications that improve the interaction between the allo-phane and the cementitious matrix, preserving its surface area and porous structure.

2.1.2. Scanning and Transmission Electron Microscopy (SEM and TEM)

Two electron microscopy techniques were used for the structural and morphological characterization of the material: the transmission electron microscope (FEI Tecnai Spirit Twin, 120 kV) and the scanning electron microscope (Tescan MIRA 3). Both analyses were performed at CENCINAT, the Nanomaterials Characterization Laboratory of the University of the Armed Forces—ESPE. The analyses were conducted on sieved additive samples using mesh sizes 40, 140, and 325.

2.1.3. Allophane Particle Size Measurements

To evaluate the nanometric nature of the additive, several particles in the three samples were measured to estimate their approximate diameters. Fiji: ImageJ software and the images from the TEM analysis were used for this purpose. The measurement scale matched that used in the microscopy technique.

2.1.4. BET Analysis

To determine the surface characteristics of allophane and its adsorption capacity, its specific surface area was measured by BET analysis using a chemisorption analyzer. To account for the material's particle-size diversity, the same samples, split into different particle-size fractions for microscopy analyses, were analyzed again. Prior to these measurements, the samples were heat-activated at 180°C to degas them and remove adsorbed water and surface hydroxyl groups, ensuring a more reliable and representative analysis of the allophane structure. The test was conducted in accordance with ASTM E11 [15].

2.1.5. Optimization Model

Based on the experimental absorption percentages, two optimization models were developed to determine the allophane dosage that minimizes water absorption in the mortar. This was accomplished by identifying the best combinations of variables: sand-to-cement ratio, additive concentrations, water absorption, and curing ages (Table 1).

Table 1. Percentage absorption results at both ages.

| Ratio | Additive (%) | Absorption (%) | |
|-------|--------------|----------------|---------|
| | | 7 days | 28 days |
| 1:3 | 0 | 0.261 | 0.357 |
| | 0.5 | 0.202 | 0.567 |

Continued

| | | | |
|-----|-------|-------|-------|
| | 1 | 0.255 | 0.641 |
| | 1.5 | 0.144 | 0.513 |
| | 2 | 0.436 | 0.836 |
| | 1.5 C | 0.687 | 0.935 |
| | 0 | 0.815 | 0.538 |
| | 0.5 | 0.868 | 0.851 |
| 1:4 | 1 | 0.803 | 0.792 |
| | 1.5 | 0.555 | 0.672 |
| | 2 | 0.437 | 0.709 |
| | 1.5 C | 0.857 | 1.238 |
| | 0 | 0.8 | 0.742 |
| | 0.5 | 0.766 | 0.571 |
| 1:5 | 1 | 0.878 | 0.688 |
| | 1.5 | 0.736 | 0.686 |
| | 2 | 0.711 | 0.699 |
| | 1.5 C | 1.306 | 0.892 |

Source: [4].

The model was developed using the Python programming language. Two approaches were considered: one based on a discrete-data method and the other on a minimization technique using cubic spline interpolation.

1) Discrete Data Optimization Model

This model is based on experimental data and seeks the optimal combination that minimizes absorption.

Model Equation

The model's objective equation is given by:

$$Z = \sum_{i=1}^n \sum_{j=1}^m A_{ij} * x_{ij} \quad (1)$$

where:

Z : Is the total minimum absorption (model objective, to be minimized).

A_{ij} : Is the water absorption value for ratio i and additive percentage j , at a specific curing time (7 or 28 days).

x_{ij} : Binary variable.

i ratio: Represents the cement-to-sand (1:3, 1:4, and 1:5) proportions.

j percentages: Represent the evaluated additive percentages (0%, 0.5%, 1%, 1.5%, and 2%).

Restrictions

The model will consider two constraints:

- Each cement-to-sand ratio: must select exactly one percentage of additive.

$$\sum_{j=1}^m x_{ij} = 1 \quad \forall i, j \quad (2)$$

- x_{ij} is binary, meaning that only one percentage of the additive will be selected from among the experimental values

$$x_{ij} \in \{0,1\} \quad (3)$$

2) Minimization Optimization Model with Cubic Spline

Based on experimental data, the model uses cubic splines for interpolation, allowing it to fit the absorption curves. It also facilitates comparing these fits with the minimum values obtained directly from the tests.

Minimize the absorption value evaluated in the cubic spline.

$$S(x), \text{ where } S(x) \text{ is the fitted cubic spline} \quad (4)$$

The percentage of the additive must be within the range of experimental values.

$$x \in \{x_{\text{beginning}}, x_{\text{end}}\} \quad (5)$$

where:

- $X_{\text{beginning}}$: Lower additive percentage (0%).
- X_{end} : Higher additive percentage (2%).

Model approaches

Focus 1

The model searches directly from the experimental data for the optimal combination that minimizes water absorption in the mixture.

$$X_{\min} = \arg \min_{x \in \{x_1, x_2, \dots, x_n\}} f(x) \quad (6)$$

where:

X_{\min} : Percentage of additive that minimizes water absorption.

arg min: Argument to search for.

$x \{x_1, x_2, \dots, x_n\}$: Percentages of experimental additive.

$f(x)$: Absorption corresponding to x_i .

Focus 2

The model uses a continuous function fitted to the experimental data to find minimum points via third-degree polynomial (cubic spline) interpolation. This allows more accurate solutions to be identified between the experimental points.

$$X_{\min} = \arg \min_{x \in \{x_{\text{start}}, x_{\text{end}}\}} S(x) \quad (7)$$

$$S(x) = \begin{cases} a_1x^3 + b_1x^2 + c_1x + d_1, & x_1 \leq x < x_2 \\ a_2x^3 + b_2x^2 + c_2x + d_2, & x_2 \leq x < x_3 \\ \vdots & \\ a_nx^3 + b_nx^2 + c_nx + d_n, & x_{n-1} \leq x < x_n \end{cases} \quad (8)$$

where:

X_{\min} : Percentage of additive that minimizes water absorption.

arg min: Argument to search for.

$x [x_{\text{start}}, x_{\text{end}}]$: Continuous range within the additive percentage interval.

$S(x)$: Cubic spline (combination of cubic polynomials).

a_b, b_b, c_b, d_b : Coefficients of the polynomial in interval $[x_b, x_{b+1}]$.

The spline will be defined by four segments corresponding to the domain interval, that is, the additive percentages between [0% - 2%], and the function $S(x)$ changes from one cubic polynomial to another as it moves from one interval to the next.

2.2. Asphalt Analysis

The research focused on the experimental and comparative assessment of how allophane influences the properties of asphalt mixtures, in accordance with national and international standards for material characterization and mixture design. Among the experimental stages are the characterization of the raw materials (AC-20 asphalt and stone aggregates), conducting control tests to verify the mix design, and evaluating the performance of conventional versus allophane-modified asphalt mixtures.

2.2.1. Materials

Among the materials that make up the asphalt mixtures are: 1) AC-20 asphalt from the Esmeraldas State Refinery, Ecuador, sampled directly from the storage tank at 150 °C, ensuring its purity and representativeness. 2) Allophane, a nanoclay of volcanic origin, incorporated into the modified asphalt mixtures at an optimal dosage of 5% by weight of the asphalt binder, which corresponds to approximately 0.25% by total weight of the asphalt mixture, according to the mixture design adopted in this study. And 3) stone aggregates, with a composition of 25% coarse aggregate $\frac{3}{4}$ ", 25% medium aggregate $\frac{1}{2}$ ", and 50% fine aggregate-sand.

2.2.2. Design and Preparation of Hot Mix Asphalt

Conventional and hot-mix asphalt mixtures containing 5% allophane were prepared using the Marshall method, with a base mix design of 95.1% crushed stone aggregate and 4.9% AC-20 asphalt. For preparing test briquettes, appropriate mixing and compaction temperatures were identified for each mixture type, ensuring adherence to the design and gradation standards (**Table 2**).

Table 2. Design and preparation of asphalt mixtures.

| Property | Conventional Asphalt Mixtures | Modified Asphalt Mixtures |
|----------------------------|-------------------------------|---------------------------|
| Mixing temperature, °C | 160 | 170 |
| Compaction temperature, °C | 150 | 160 |
| Mixture dosages | 95.1% Stone aggregates | 95.1% Stone aggregates |
| | 4.9% AC-20 asphalt | 4.655% AC-20 asphalt |
| | | 0.245% Allophane |

Source: [9].

The selection of the allophane concentration was based on prior experimental evidence reported in the literature and on the preliminary analysis developed in the framework of this research. According to Espinoza and Valdivieso (2019), an allophane content of 5% by weight of asphalt binder represents an optimal dosage, as it improves the mechanical performance of asphalt mixtures without adversely affecting their volumetric properties or workability. Considering that the asphalt content in the designed mixtures is 4.9% by total weight of the mix, this proportion corresponds to an effective allophane concentration of approximately 0.25% relative to the total mixture mass. Therefore, this dosage was adopted in the present study to ensure consistency with validated findings and to allow a reliable comparative evaluation between conventional and allophane-modified asphalt mixtures.

2.2.3. Asphalt Mixtures Aging

To evaluate durability, the mixtures were conditioned in the short and long term according to AASHTO R-30 standards, considering that short-term aging simulates conditions during construction and the first years of service (3 to 5 years); while long-term aging predicts behavior after several years (7 to 10 years) of environmental and traffic exposure [16].

2.2.4. Tests and Characterization

Tests were carried out to characterize the physical-mechanical and rheological properties of the asphalt mixtures, essentially:

1) Volumetric properties: To verify that the asphalt mixture design complies with the permitted ranges, include the maximum theoretical specific gravity RICE (Gmm), the specific gravity of the compacted BULK mixture (Gmb), the percentage of air voids (Va), voids in the mineral aggregate (VMA), and asphalt-filled voids (VFA).

2) Stability and Marshall Flow: The stability and flow of the briquettes were assessed according to ASTM D 6927.

3) Indirect Traction/Rigidity Modulus: Non-destructive indirect tensile strength tests were conducted to determine the rigidity modulus at 10°C, 20°C, and 40°C. These tests measure the axial deformation of cylindrical specimens under repeated loads, using a universal hydraulic dynamic testing machine that simulates vehicular conditions.

4) Cantabrian Wear: Wear loss was determined using the Cantabro test. The test was performed with briquettes conditioned at 25°C, without an abrasive load in the Los Angeles machine, and the sample weight was compared before and after 300 revolutions.

5) Fourier Transform Infrared Spectroscopy (FTIR): FTIR was performed to analyze the chemical composition of allophane and conventional and modified asphalt mixtures, including aged samples.

6) Thermogravimetric Analysis (TGA): TGA was performed to evaluate the thermal stability of allophane and asphalt mixtures, including aged samples.

3. Results and Discussion

3.1. Mortar Analysis

3.1.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) micrographs show that allophane has a morphology characterized by particles lacking a defined crystalline arrangement, confirming its amorphous nature (**Figures 1-3**). This behavior matches that of aluminum silicate-based materials [17], which typically exhibit heterogeneous, rough surfaces. Allophane and other clay-derived nanomaterials exhibit a wide range of morphologies, from one-dimensional to three-dimensional, endowing them with excellent adsorption properties [18].

The absence of a regular crystalline network favors a larger specific surface area and the potential for stronger interactions with the cementing matrix. These properties allow allophane to disperse more uniformly, forming a solid interface that enhances the adhesion and mechanical resistance of the construction materials in which it is incorporated.

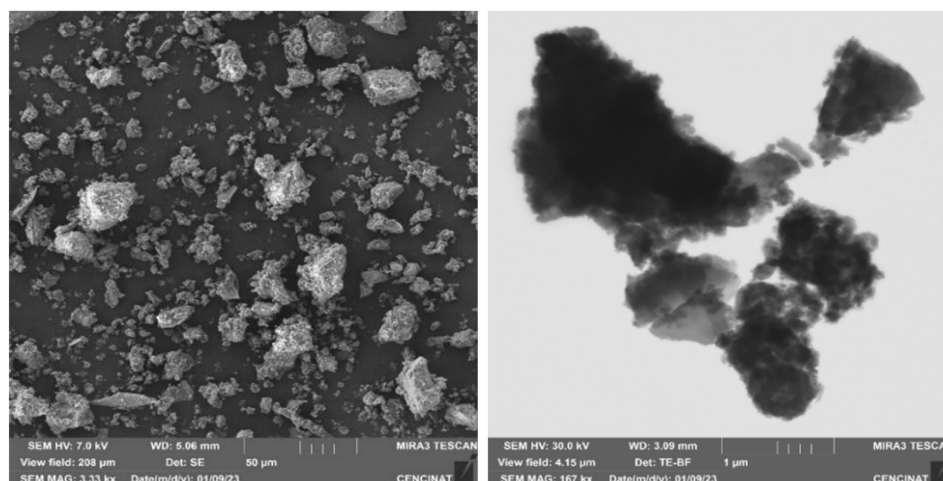


Figure 1. SEM: Allophane sample (45 µm) at a scale of 50 µm and 1 µm.

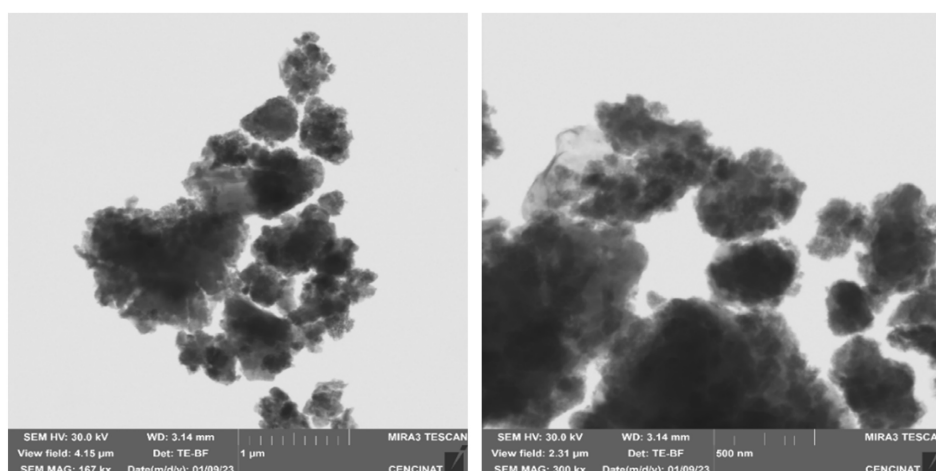


Figure 2. SEM: Allophane sample (106 µm) at a scale of 1 µm and 500 nm.

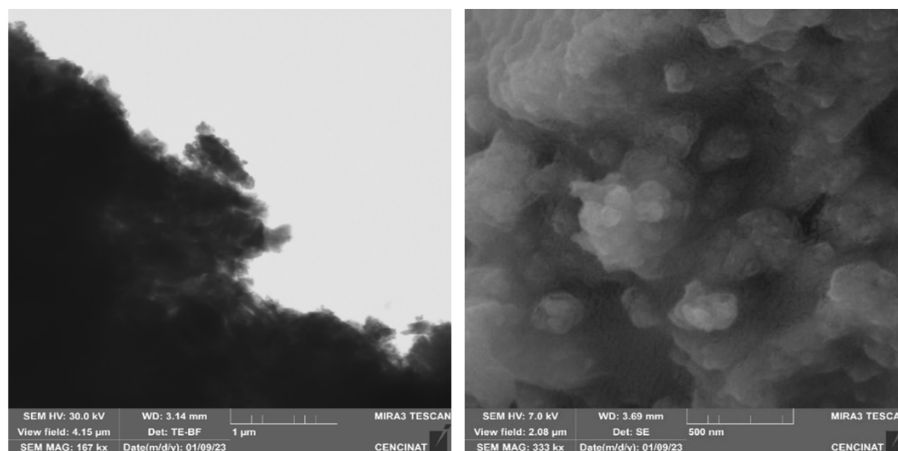


Figure 3. SEM: Allophane sample (425 µm) at a scale of 1 µm and 500 nm.

3.1.2. Transmission Electron Microscopy (TEM)

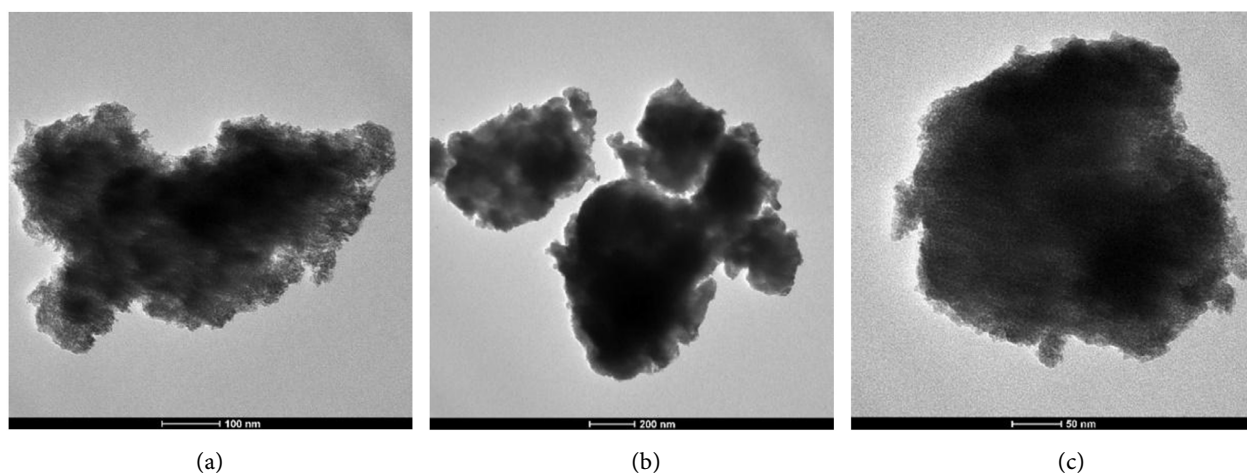


Figure 4. (a) Allophane sample (45 µm) at 100 nm scale. (b) Allophane sample (106 µm) at 50 nm scale. (c) Allophane sample (425 µm) at 50 nm scale.

Analysis using transmission electron microscopy (TEM) revealed the organization of allophane at the nanoscale, identifying nanoparticles that tend to cluster into irregular domains (Figure 4). The measured external diameters are within a few nanometers, which is consistent with the previously reported dimensions for this type of amorphous phyllosilicate [19]. The particles exhibit a tubular or spheroidal morphology [20], which favors the formation of larger aggregates and enhances the material's structural stability. The lack of a well-defined crystalline pattern confirms its amorphous nature and is consistent with observations in SEM. A relevant aspect is the discrepancy between the absence of noticeable pores in the TEM micrographs and the high specific surface area determined by BET analysis, which is explained by the difficulty of this technique in visualizing microporosity or mesopores in non-crystalline materials. This methodological complementarity underscores the importance of combining diverse characterization techniques to fully understand the nature of allophane.

3.1.3. Particle Size

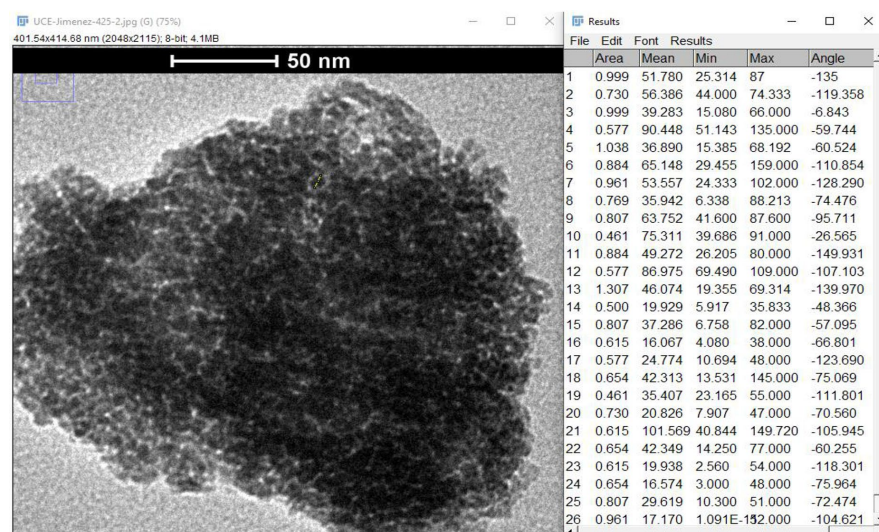


Figure 5. Measurement of allophane particles in ImageJ.

The particle size analysis obtained from the TEM micrographs showed (Figure 5) that the allophane is made up of particles in the nanometer range, with diameters between approximately 3.2 and 3.8 nm, according to the particle measurements in the Fiji software: ImageJ of images obtained in TEM analysis with physical separations of 45, 106, and 425 μm . This coincides with previous characterization reports. Although no defined pores are visible in the TEM images, the BET adsorption results confirm the presence of micropores with diameters less than 1 nm, which support the material's nanoparticulate nature and specific surface area. These properties are decisive in improving its interaction capacity and performance in construction applications.

3.1.4. BET Analysis

The BET analysis results showed that the used allophane has a porous structure capable of gas adsorption, as indicated by its specific surface areas of 46.614, 81.537, and 45.006 m^2/g for the 45, 106, and 425 μm particle size fractions, respectively. Although these areas are lower than those of highly porous materials such as zeolites (which can exceed 500 m^2/g), they still indicate a structure with accessible porosity. The amorphous nature of allophane prevents these pores from being directly observed by electron microscopy (SEM or TEM); however, BET analysis allows us to infer the presence of an active, accessible surface, confirming its porous characteristics.

The porous structure of allophane provides it with beneficial properties as an additive in construction materials. Its incorporation into mortar or concrete mixes could enhance the physicochemical interactions among the components, thanks to the increased available surface area. Additionally, this feature could promote higher water retention in the cementitious matrix, which aids internal curing of the material. This capacity to act as a moisture reservoir can help sustain

more stable hydration conditions. Moreover, allophane can influence the material's capillary network, affecting water movement within the system and restricting deep penetration, thereby improving performance during humidity cycles.

3.1.5. Discrete Data Optimization Model Simulation Results

```

Objective value:          1.55050000
Enumerated nodes:        0
Total iterations:         0
Time (CPU seconds):      0.00
Time (Wallclock seconds): 0.01

Option for printingOptions changed from normal to all
Total time (CPU seconds): 0.01 (Wallclock seconds): 0.02

Resultados óptimos por relación y tiempo de curado:
Relación 1:3:
- 7 días: Porcentaje de aditivo óptimo: 1.5%, Absorción: 0.144
- 28 días: Porcentaje de aditivo óptimo: 0%, Absorción: 0.357
Relación 1:4:
- 7 días: Porcentaje de aditivo óptimo: 2%, Absorción: 0.437
- 28 días: Porcentaje de aditivo óptimo: 0%, Absorción: 0.538
Relación 1:5:
- 7 días: Porcentaje de aditivo óptimo: 2%, Absorción: 0.712
- 28 días: Porcentaje de aditivo óptimo: 0.5%, Absorción: 0.571

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Note. The comparison of the values obtained in the simulation with the experimental values can be found in [Table 3](#) and [Table 4](#).

Figure 6. Simulation of the optimization model with discrete data.

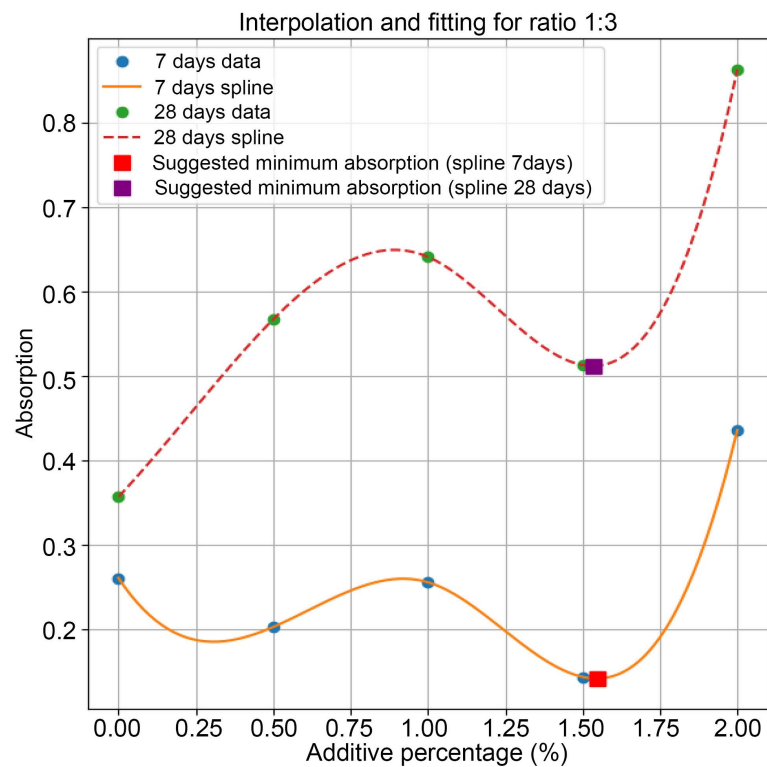
The experimentally obtained water absorption results can be interpreted using the discrete optimization model, defined by the objective function Z , where A_{ij} represents the observed absorption for each combination of ratio and additive concentration, and x_{ij} is the decision variable indicating the selection of that combination ([Figure 6](#)). This approach shows that the most efficient combination (*i.e.*, 1:5 ratio with 0.5% additive) is the one that minimizes the value of x_{ij} and consequently the function Z , representing the lowest total absorption among the samples evaluated. Interestingly, higher additive concentrations or partial replacement with cement do not lead to reduced absorption, indicating that the objective function is not monotonic with respect to concentration and that there is a complex interaction between the mix ratio and additive dosage. This analysis not only helps identify the optimal dosage but also measures how each variable combination influences the property of interest, aiding decision-making based on objective mathematical criteria. This allows you to experimentally connect the data to the mathematical model, demonstrating that the lowest absorption corresponds to the minimum of Z predicted by the model. Notably, increasing additive concentrations does not necessarily improve performance and can sometimes increase absorption, due to saturation or interference effects in the mortar's microstructure, suggesting the existence of such saturation or interference effects. On the other hand, the inclusion of cement instead of the additive (1.5% C) systematically produces higher absorptions than the standard across all ratios, indicating that cement does not mimic the additive's properties and that its specific incorporation

helps reduce the material's capillarity. These findings demonstrate that both the amount of additive and its interaction with the cement-to-sand ratio significantly influence the final behavior when exposed to water. These details facilitate a discussion about how additive concentration and mix ratio interact.

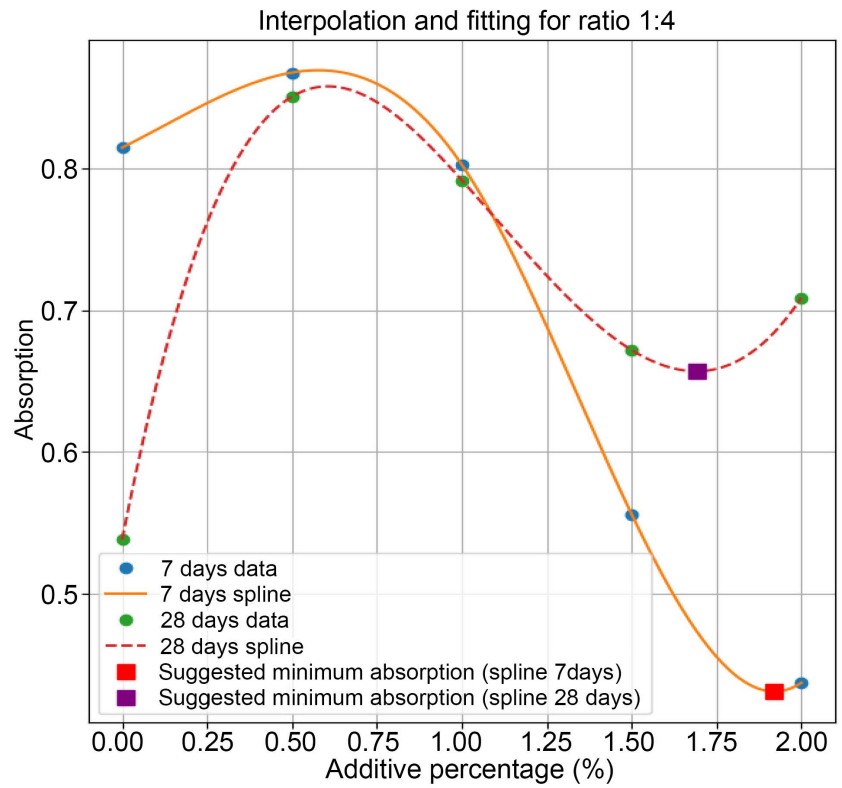
3.1.6. The Simulation Results of the Minimization Optimization Model with Cubic Splines Discrete Data Optimization Model Simulation Results

The application of the cubic spline model allowed us to estimate the minimum water absorption achievable across the continuous range of allophane concentrations, beyond the specific values measured experimentally. According to equation $X_{\min} = \arg S(x)$, the optimal additive concentration that results in the lowest absorption predicted by the adjusted curve was identified (Figure 7).

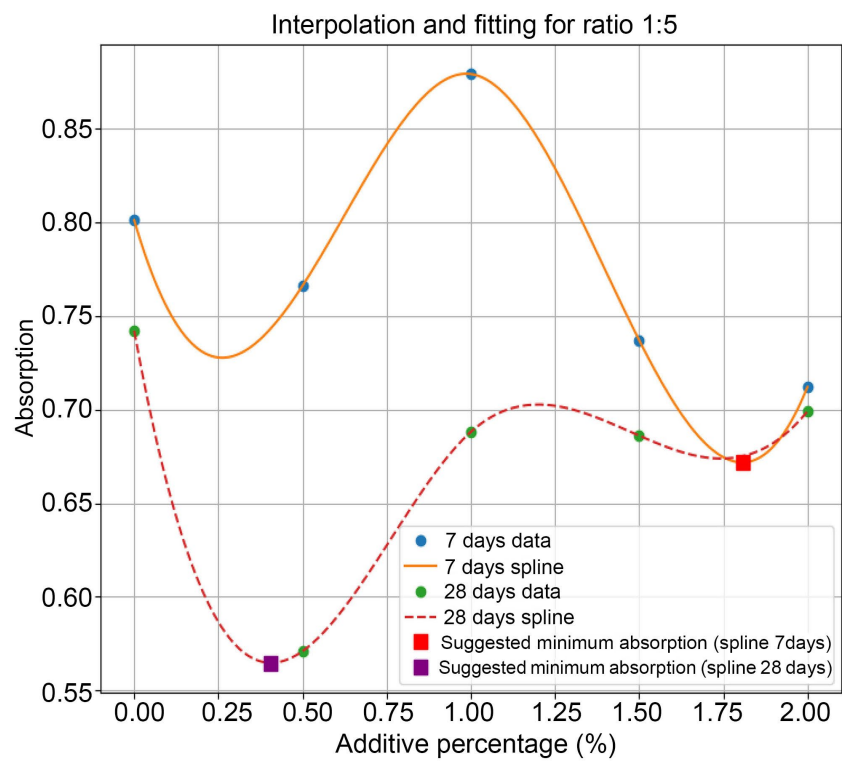
The slight discrepancies observed between the experimentally determined optimum dosages and those predicted by the cubic spline interpolation model (Table 3 and Table 4) have relevant practical implications from an engineering perspective. These differences reflect the model's ability to smooth the system's response and capture the overall trend of mortar behavior with respect to allophane incorporation. The spline approach does not identify a single, rigid optimum point, but rather defines effective dosage ranges within which absorption remains controlled. This behavior is particularly advantageous for field conditions, where the variability of materials, curing processes, and construction procedures makes it impossible to exactly replicate laboratory conditions.



(a)



(b)



(c)

Figure 7. Absorption (%) vs. Concentration (%): Cubic splines for the different ratios and two curing ages. ratio 1:3; b) ratio 1:4; and c) ratio 1:5.

Table 3. Percentage of additive suggested by the Cubic Spline for 7 days of curing.

| Ratio | 7 days of curing | | | |
|-------|------------------|----------------|--------------|----------------|
| | Experimental | | Spline | |
| | Additive (%) | Absorption (%) | Additive (%) | Absorption (%) |
| 1:3 | 1.5 | 0.144 | 1.55 | 0.1421 |
| 1:4 | 2 | 0.437 | 1.92 | 0.4308 |
| 1:5 | 2 | 0.712 | 1.81 | 0.6717 |

Note. The model adjusts the data to produce a continuous, smooth representation, which may yield optimal values that differ from the experimental ones.

Table 4. Percentage of additive suggested by the Cubic Spline for 28 days of curing.

| Ratio | 28 days of curing | | | |
|-------|-------------------|----------------|--------------|----------------|
| | Experimental | | Spline | |
| | Additive (%) | Absorption (%) | Additive (%) | Absorption (%) |
| 1:3 | 0 | 0.357 | 1.53 | 0.5119 |
| 1:4 | 0 | 0.538 | 1.69 | 0.6570 |
| 1:5 | 0.5 | 0.571 | 0.41 | 0.5648 |

In particular, for a 1:5 cement:sand ratio at 28 days, the model suggests an optimum dosage of 0.41% compared to the experimental 0.5%, while maintaining comparable absorption values. This confirms the existence of a zone of efficient performance rather than a single, strictly defined value.

The benefit of this method is its ability to explore a continuous range of concentrations, analyze trends, and support decisions on fine-tuning the mortar formulation to reduce capillarity.

3.2. Asphalt Analysis

The results obtained enabled a detailed comparison between conventional asphalt mixtures and those modified with allophane, both in their normal state and after aging processes. It should be noted that the materials were characterized before preparing the asphalt mixtures. The AC-20 asphalt used met the quality specifications and was deemed suitable. The modification focused on adding natural allophane, a volcanic nanomaterial.

3.2.1. Volumetric Properties of Asphalt Mixtures

The maximum theoretical specific gravity (RICE, Gmm), the specific gravity of the compacted mixture (BULK, Gmb), the percentage of air voids (Va), the percentage of absorbed asphalt (Pba), the percentage of effective asphalt (Pbe), the percentage of voids in the mineral aggregate (VMA), and the percentage of voids filled with asphalt (VFA) were analyzed. These indicators are crucial for the quality and performance of asphalt mixtures (**Table 5**).

Table 5. Results of volumetric properties of asphalt mixtures.

| Condition | Property | Conventional Asphalt Mixtures | Modified Asphalt Mixtures | Percentage Improvement |
|-----------|---|-------------------------------|---------------------------|------------------------|
| NA | Maximum theoretical specific gravity RICE, Gmm | 2.420 | 2.432 | 0.496 |
| STA | | 2.428 | 2.440 | 0.494 |
| LTA | | 2.416 | 2.428 | 0.497 |
| NA | Specific gravity of the compacted BULK mixture, Gmb | 2.311 | 2.331 | 0.865 |
| STA | | 2.317 | 2.343 | 1.122 |
| LTA | | 2.337 | 2.342 | 0.214 |
| NA | Percentage of air voids (%Va) | 4.766 | 4.409 | 7.491 |
| STA | | 4.849 | 4.239 | 12.580 |
| LTA | | 3.564 | 3.835 | 7.604 |
| NA | % Voids in the mineral aggregate, (VMA) | 14.690 | 13.952 | 5.024 |
| STA | | 14.487 | 13.518 | 6.689 |
| LTA | | 13.752 | 13.576 | 1.280 |
| NA | % Asphalt-filled voids, (VFA) | 67.554 | 68.398 | 1.249 |
| STA | | 66.530 | 68.64 | 3.172 |
| LTA | | 74.085 | 71.749 | 3.153 |
| NA | % Absorbed asphalt (PBA) | 0.459 | 0.672 | 46.405 |
| STA | | 0.601 | 0.814 | 35.441 |
| LTA | | 0.388 | 0.601 | 54.897 |
| NA | % Effective asphalt (PBE) | 4.464 | 4.261 | 4.547 |
| STA | | 4.328 | 4.126 | 4.667 |
| LTA | | 4.531 | 4.328 | 4.480 |

Note. The condition of the samples refers to: NA = Non-aged, STA = Aged short-term, and LTA = Long-term aged.

The incorporation of allophane into asphalt mixtures significantly impacted their volumetric properties, both in their initial state and after aging processes, reflecting a positive interaction with the asphalt binder and the aggregates. In General, it was observed that the Theoretical Maximum Specific Gravity (Gmm) of the modified mixtures increased slightly by 0.495% due to the higher density of the allophane compared to air or voids. Consequently, the Bulk Specific Gravity (Gmb) also showed a tendency to increase by 0.733% in the mixtures containing allophane, which is attributed to better compaction and a denser structure. (ASTM D 2726, 2019). This improvement in compacted density correlates with a 9.224% decrease in Air Void Percentage (Va) in the modified mixtures, which is highly desirable since fewer voids imply greater resistance to water and air entry, reducing susceptibility to aging and moisture damage.

The porous nature and high specific surface area of allophane influenced the Percentage of Asphalt Absorbed (Pba), which increases by 45.58% in the modified

mixtures due to this nanomaterial's ability to absorb and retain part of the binder. Despite this increase in Pba, the Percentage of Effective Asphalt (Pbe) tends to stay stable, indicating that allophane helps improve the distribution and fixation of the asphalt available for cohesion. Regarding Voids in the Mineral Aggregate (VMA), a slight decrease or stability of 4.33% was observed in the modified mixtures, suggesting that allophane occupies space within the aggregate matrix without compromising the asphalt film.

Finally, the Asphalt-Filled Voids (AFV) of the mixtures with allophane showed a tendency to increase by 2.52%, validating the optimization of the space between aggregates when filled with a binder and allophane mixture. This results in a more compact mixture with lower permeability, which has direct implications for greater durability and better protection against long-term oxidation. These trends were maintained or even accentuated in the aged mixtures, suggesting that allophane helps mitigate the volumetric degradation that typically occurs over time and with environmental exposure.

3.2.2. Marshall Stability and Flow

The Marshall test is one of the most fundamental and widely used tests in pavement engineering for the design and quality control of asphalt mixtures. Its importance lies in its ability to determine two key properties that govern the mechanical behavior of the mixture under traffic loads: Marshall Stability and Marshall Flow.

Marshall Stability represents the maximum load that a cylindrical test specimen of compacted asphalt mixture (briquette) can withstand before significant plastic deformation occurs. In other words, it is a direct measure of the mixture's resistance to permanent deformation under heavy, repetitive traffic. High stability is crucial to maintaining the pavement's shape and structural capacity throughout its service life.

On the other hand, Marshall Flow measures the vertical plastic deformation of the test specimen from the start of loading to the point of maximum stability. This value indicates the mixture's flexibility, or its ability to deform without fracturing. Too low a flow may indicate a fragile mixture susceptible to fatigue cracking. At the same time, an excessively high flow indicates a mixture that is too yielding and prone to excessive deformation under load. The optimal combination of stability and flow ensures adequate performance in the field (**Table 6**).

Table 6. Marshall Criteria for heavy traffic.

| Traffic Type | Heavy | | | |
|----------------------|---------------|------|-------------------|------|
| | MOP-001F-2002 | | Asphalt Institute | |
| Marshall Criteria | Min. | Max. | Min. | Max. |
| N° of blows/side. | 75 | | 75 | |
| Stability, (pounds). | 1800 | - | 1800 | - |
| | (817 kg) | | (8006 N) | |

Continued

| | | | | |
|--|-----|-----|----|----|
| Flow, (inches/100). | 8 | 14 | 8 | 14 |
| Percentage of voids in the mixture, %Va. | 3 | 5 | 3 | 5 |
| Percentage of voids in the mineral aggregate, VMA. | 13 | 15 | 13 | 15 |
| Percentage of voids filled with asphalt, VFA. | 65 | 75 | 65 | 75 |
| Filler/bitumen ratio. | 0.8 | 1.2 | - | - |

Note. The table shows the technical specifications of both MOP-001F-2002 at the local level and the Asphalt Institute at the international level. Adapted from [11] and [21].

The Marshall Stability and Flow results, presented in **Table 7**, demonstrate the positive impact of allophane as a modifier in asphalt mixtures, especially in its ability to resist traffic loads and deformation.

Table 7. Marshall stability and flow results of asphalt mixtures.

| Condition | Property | Conventional Asphalt Mixtures | Modified Asphalt Mixtures | Percentage Improvement |
|-----------|--------------------|-------------------------------|---------------------------|------------------------|
| NA | Marshall Stability | 2081.88 | 2997.23 | 43.967 |
| STA | | 2348.94 | 2903.49 | 23.609 |
| LTA | | 2972.55 | 4001.15 | 34.603 |
| NA | Marshall Flow | 9.67 | 10 | 3.413 |
| STA | | 12.33 | 12 | 2.676 |
| LTA | | 12 | 12 | - |

Note. The condition of the samples refers to: NA = Not aging, STA = Short-term aging, and LTA = Long-term aging.

Research indicates that Marshall Stability improved markedly in all-allophane-modified mixtures across various conditions. Under the non-aged condition (NA), the modified mixture's stability reached 2997.23, a 43.97% rise from the conventional mix. During short-term aging (STA), the stability of the modified mix remained substantially higher at 2903.49 compared to 2348.94 in the conventional, marking a 23.61% increase. In long-term aging (LTA), the modified mixture achieved a stability of 4001.15, reflecting a 34.60% improvement over the conventional mix (**Figure 8**).

This constant improvement in stability, with an average improvement of 34.06% across all conditions, indicates that allophane significantly enhances the rigidity and intrinsic resistance of the mixture against permanent deformations induced by traffic. The high surface specificity of allophane and its ability to absorb and reinforce the asphalt binder create a more resistant and cohesive matrix, which translates into a greater capacity to withstand vertical loads. This increase is crucial for pavement durability, minimizing rutting and structural deterioration.

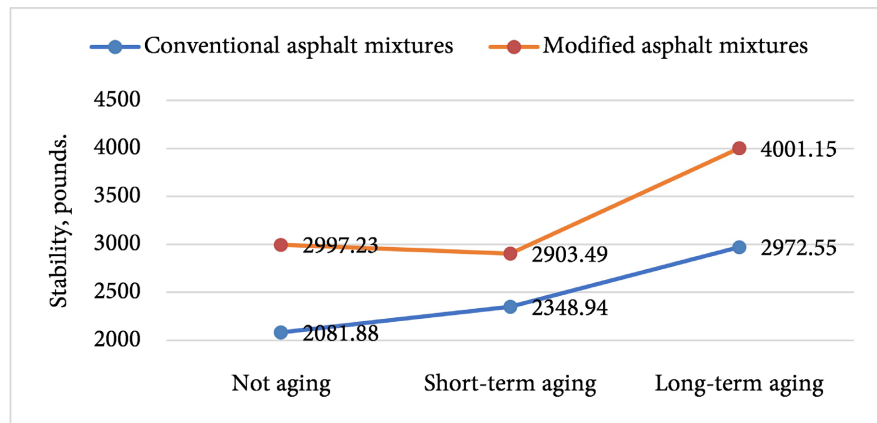


Figure 8. Comparative Marshall stability graph.

Regarding Marshall flow, the results suggest that allophane contributes to a mixture with controlled deformability. In non-aged condition (NA), the flow of the modified mixture was 10, slightly higher than the 9.67 of the conventional mixture, with an increase of 3.41%. For the short-term aging condition (SAC), the flow of the modified mixture was 12, while that of the conventional mixture was 12.33, representing a slight decrease of 2.68%. Finally, in the long-term aging condition (LAP), both mixtures had a flow of 12, with no difference observed.

The average percentage improvement in flow was 3.04%, indicating that, although stability increased significantly, flow stayed within acceptable ranges or even slightly decreased under aging conditions. This is positive because a minor change in flow without a large drop in stability suggests that the mixture remains flexible enough to resist fatigue while gaining greater resistance to deformation. Allophane thus provides a favorable balance between strength and flexibility, without making the mixture overly brittle despite its increased rigidity (Figure 9).

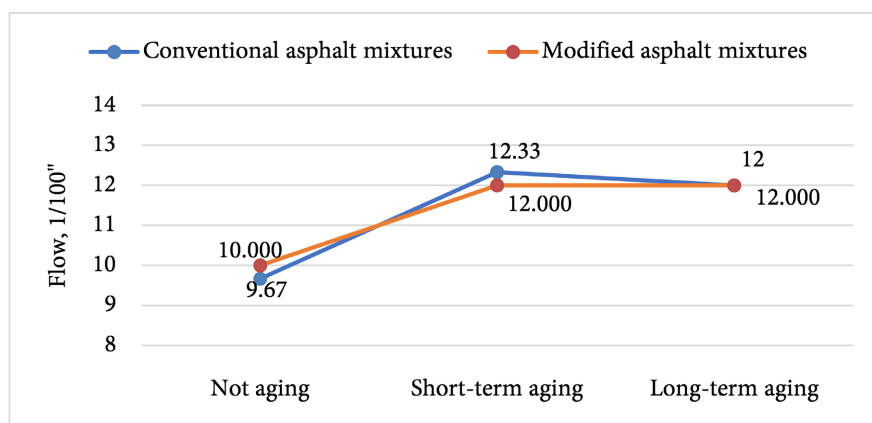


Figure 9. Comparative Marshall flow graph.

In summary, the addition of allophane substantially improves the asphalt mixture's ability to withstand traffic loads by significantly increasing its Marshall Sta-

bility, which is essential for preventing plastic deformation. At the same time, Marshall Flow remains within desirable ranges, indicating that this increased rigidity does not compromise the mixture's ability to deform minimally without cracking. These results demonstrate that allophane not only provides greater initial strength but also helps maintain superior mix performance even after aging, thereby extending the service life of flexible pavement.

3.2.3. Rigidity Module—Indirect Traction

The Indirect Tensile Test is a crucial non-destructive mechanical test for evaluating the tensile strength of asphalt mixtures, which is directly related to the pavement's ability to resist fatigue cracking and the formation of shallow fissures. This test allows the determination of the dynamic Rigidity Modulus, a fundamental parameter that describes the relationship between stress and strain of the mixture under repetitive traffic loads. The rigidity modulus is a vital indicator of the mixture's ability to distribute applied loads, resist elastic deformation, and ultimately prevent cracking. The importance of this test lies in its ability to simulate the tensile stresses induced in the lower part of an asphalt layer by vehicle passage, which is a common failure mechanism in pavements. Furthermore, being performed at different temperatures allows the thermal sensitivity of the mixture and its behavior to be evaluated across a range of climatic conditions, from cold temperatures, where the mixture is more rigid and prone to cracking, to warm temperatures, where it may be more susceptible to deformation. The results of the indirect tensile tests—rigidity modulus (**Table 8**) show that the incorporation of allophane significantly improved the stress-strain relationship of the asphalt mixtures, increasing their rigidity and tensile strength, and that this positive effect was maintained, and even accentuated, after the aging processes.

Table 8. Indirect tensile test results/rigidity module.

| Condition | Property | Conventional Asphalt Mixtures | Modified Asphalt Mixtures | Percentage Improvement |
|-----------|---------------------------------------|-------------------------------|---------------------------|------------------------|
| NA | Indirect tensile to 20°C | 2765.65 | 3505.15 | 26.739 |
| STA | | 2768.15 | 3589 | 29.653 |
| LTA | | 4387.42 | 6263.6 | 42.763 |
| 10°C | Indirect tensile of non-aged mixtures | 5695.8 | 7002.1 | 22.934 |
| 20°C | | 2765.65 | 3505.15 | 26.739 |
| 40°C | | 505 | 629.6 | 24.673 |

Note. The test was performed on samples under the following aging conditions: NA = Non-aged, STA = Short-term aged, and LTA = Long-term aged. Temperature conditions were 10°C, 20°C, and 40°C.

When analyzing non-aged mixtures (NA) at different temperatures (10°C, 20°C, and 40°C), it is consistently observed that allophane increases the rigidity modulus and indirect tensile strength across the entire temperature range: At

10°C, the modified mixture reached a modulus of 7002.1, representing an increase of 22.93% over the conventional mixture (5695.8). This is crucial, since at low temperatures, asphalt mixtures tend to become more rigid and brittle; the improvement suggests that allophane provides greater resistance to tensile failure in cold conditions. At 20°C, the modulus of the modified mixture was 3505.15, showing a 26.74% increase over the conventional mixture (2765.65). This intermediate temperature is representative of common operating conditions, and the improvement indicates the mixture's greater ability to withstand loads without excessive deformation. At 40°C, the modified mixture exhibited a modulus of 629.6, representing a 24.67% increase compared to the conventional mixture (505). At high temperatures, asphalt mixtures become softer and more susceptible to plastic deformation. However, the fact that allophane maintains its increased rigidity at 40°C is very significant, as it indicates better resistance to permanent deformation in hot climates (**Figure 10**).

These results across different temperatures confirm that allophane not only improves the strength of the mixture but also enhances thermal stability over a wide operating range, which is essential for pavements in regions with climatic variations. The incorporation of the nanomaterial allows the mixture to maintain greater relative rigidity compared to the conventional mixture, resulting in better stress distribution and, consequently, less deformation under the same applied load.

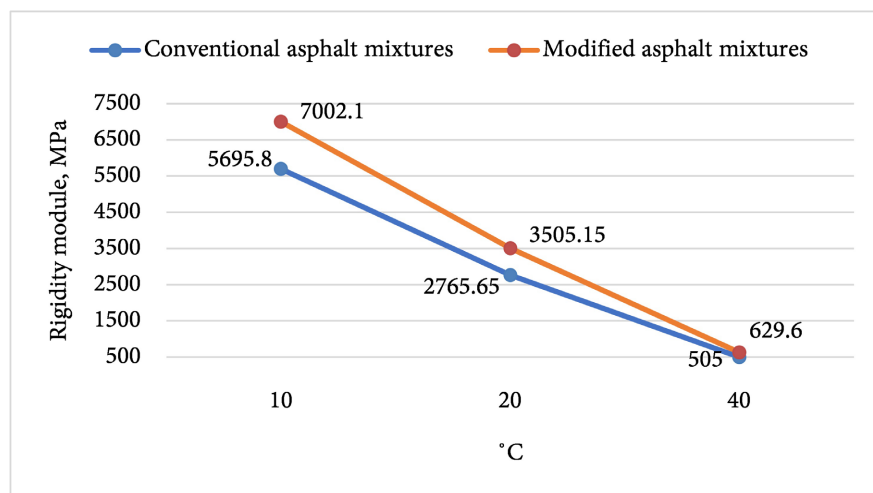


Figure 10. Comparative rigidity graph module for different temperatures.

On the other hand, the evaluation at 20°C under different aging conditions (NA, STA, LTA) shows that allophane helps mitigate the degradation of mechanical properties over time. In Non-Aging (NA), the modified mixture showed a 26.74% improvement over the conventional mix. Under short-term aging (STA) conditions, the strength of the modified mixture improved by 29.65% compared to the conventional mixture (2768.15). Surprisingly, the strength of the modified STA mixture is even slightly higher than that of the non-aged modified mixture

(3589 vs. 3505.15), which could indicate an initial curing effect of the asphalt binder in the presence of allophane. Finally, under long-term aging (LTA) conditions, the improvement becomes even more pronounced, with the modified mixture reaching an impressive 6263.6, translating into an outstanding 42.76% improvement over the conventional mixture (4387.42) (**Figure 11**).

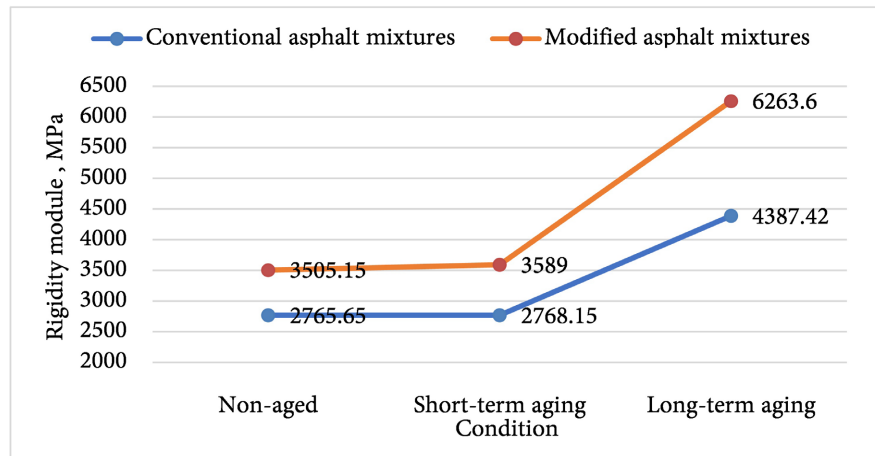


Figure 11. Comparative graph of rigidity module at 20°C.

Persistence and an increase in the percentage improvement in the rigidity modulus and tensile strength in aged mixtures confirm that allophane not only optimizes initial properties but also maintains, or even amplifies, its protective effect against oxidation degradation. This indicates that allophane improves the stress-strain relationship throughout the pavement's service life, allowing the mixture to better withstand the stresses generated by traffic and thermal changes, even after significant aging. The greater resistance observed in the LTA samples, in terms of percentage improvement, suggests that allophane acts as an agent that slows or mitigates the processes of excessive hardening and embrittlement associated with asphalt aging, thereby maintaining a more robust, resilient structure.

3.2.4. Cantabro Wear Test

The results of the Cantabro wear test indicated the abrasion resistance of the mixtures. It is a standardized test used to evaluate the resistance of asphalt mixtures to wear and surface disintegration. This test is particularly relevant for predicting the durability of a pavement against the abrasive action of traffic and environmental conditions. A low percentage of wear loss in the Cantabrian test indicates a cohesive and robust mixture, capable of maintaining its integrity under mechanical stress and weathering. On the contrary, a high wear loss suggests a mixture susceptible to aggregate disintegration and premature deterioration of the pavement surface, which would lead to a reduction in its service life and an increase in maintenance costs.

The results of the Cantabro wear test conclusively demonstrate that the incorporation of allophane significantly reduced wear loss under all aging conditions,

implying a substantial improvement in the durability of asphalt mixtures. Non-Aged (NA), the mixture modified with allophane exhibited a wear loss of 4.099%, which represents an improvement of 27.116% compared to the conventional mixture (5.624%). This indicates that, from the outset, allophane improves the cohesion and resistance of the mixture to mechanical abrasion, providing greater structural integrity. Under short-term aging conditions (STA), the protective effect of allophane is accentuated, and the modified mixture had a wear loss of 2.7531%, significantly lower than the conventional mixture (5.3541%). This translates into an impressive improvement of 48.580%. This result is fundamental, as short-term aging simulates the conditions during the construction process and the first years of pavement service, where the mix is already exposed to some oxidation. The drastic decrease in wear suggests that allophane helps preserve the mix's cohesion even in its initial stages of degradation. Finally, under long-term aging (LTP) conditions, the positive trend continues and is even more critical in long-term aged mixtures, which represent the end of the pavement's service life. The allophane-modified mixture showed a wear loss of 6.2769%, a substantial improvement compared to the 11.9258% of the conventional aged mixture. This represents a 47.367% improvement in wear loss. The ability of allophane to mitigate wear deterioration under severe long-term aging conditions is clear evidence that this nanomaterial extends pavement service life by maintaining a more compact structure less prone to aggregate disintegration, even when the asphalt binder has undergone considerable oxidation.

The consistent and significant reduction in wear loss under all aging conditions demonstrates that allophane inherently improves the durability of asphalt mixes. This improvement is attributed to allophane's ability to enhance adhesion: it strengthens the bond between the asphalt binder and the aggregates, making it more difficult for particles to separate under abrasive action; improve internal cohesion: it creates a more cohesive matrix within the mixture, making it more resistant to disintegration; and protect against aging: by mitigating oxidation and asphalt hardening, allophane helps the mix retain its ductility and cohesion, even after years of environmental exposure, which directly translates into less surface material loss.

3.2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra provided information on the chemical changes and the interaction between asphalt and allophane. To analyze the effect of allophane on the asphalt structure, the characteristic bands of the FTIR spectra are considered.

Figure 12 shows the spectrum of allophane, highlighting the band at 3450.84 cm^{-1} , which indicates the presence of O-H groups and suggests the presence of adsorbed moisture and hydroxyl groups. This is relevant because hydroxyl groups can improve the adhesion between allophane and asphalt, and the band at 1018.63 cm^{-1} is associated with the stretching of Si-O-Si or Si-O-Al bonds. This band confirms that allophane, being a silicate, can interact with asphalt, potentially improving its mechanical properties [22].

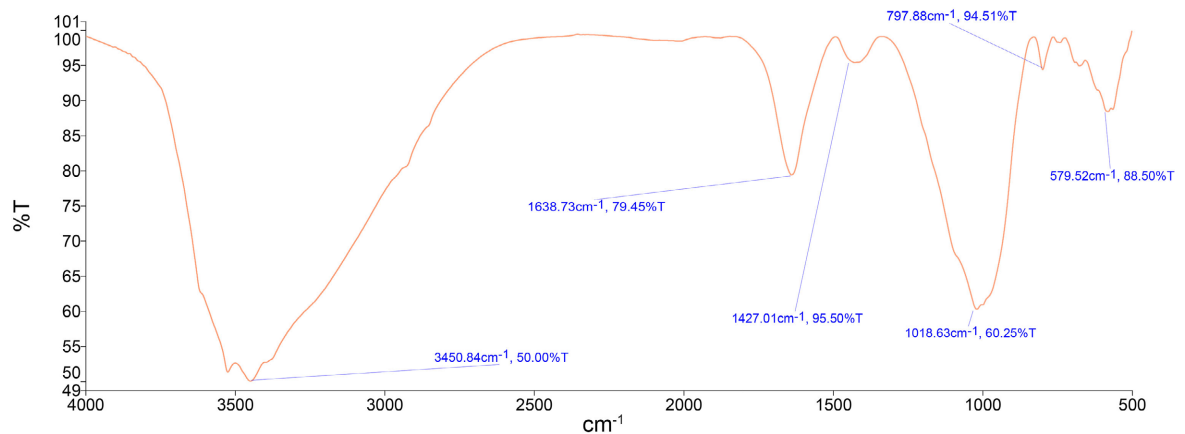


Figure 12. Allophane spectrum.

Figure 13 shows the spectrum of conventional non-aged asphalt mixtures, where the bands at 2923.63 and 2853.06 cm^{-1} , corresponding to aliphatic C-H stretches, stand out indicating the presence of hydrocarbons that make up the asphalt. The low intensity of the O-H band (3628.32 cm^{-1}) suggests that the amount of hydroxyl groups is limited, which could affect the cohesion in the mixture.

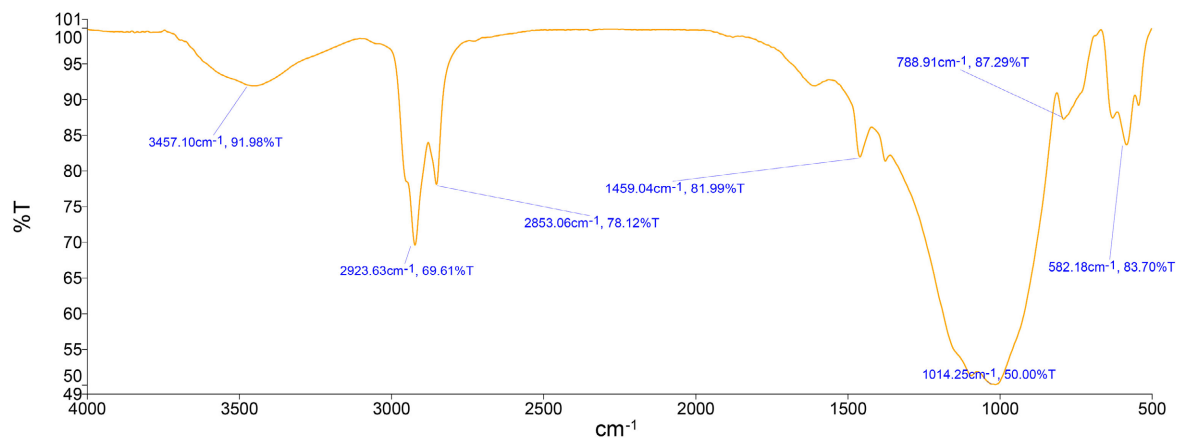


Figure 13. Spectrum of non-aged, conventional asphalt mixtures.

Figure 14 shows the spectrum of non-aged, modified asphalt mixtures, where the presence of multiple bands in the O-H region is evident, indicating that the aloe has not only been incorporated but is also interacting with the asphalt, increasing the number of hydroxyl groups. This can improve the adhesion and stability of the mixture. Furthermore, regarding the C-H bands, there is a similarity between the conventional and modified mixtures, suggesting that the asphalt's basic structure has been maintained, while allophane modification adds beneficial properties.

The spectra of conventional aged asphalt mixtures (**Figure 15**) and modified ones (**Figure 16**) show bands at 3628.32 cm^{-1} , suggesting that oxidation has reduced the amount of hydroxyl groups, which may compromise durability. However, the modified mixture shows a smaller decrease in the intensity of these

bands, indicating that the allophane could protect the asphalt from oxidation and aging.

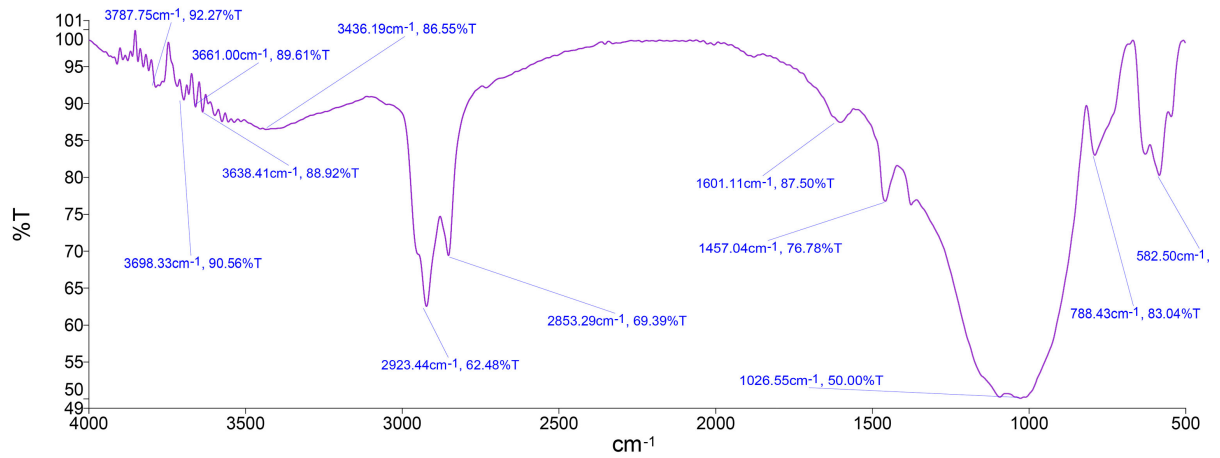


Figure 14. Spectrum of non-aged, modified asphalt mixtures.

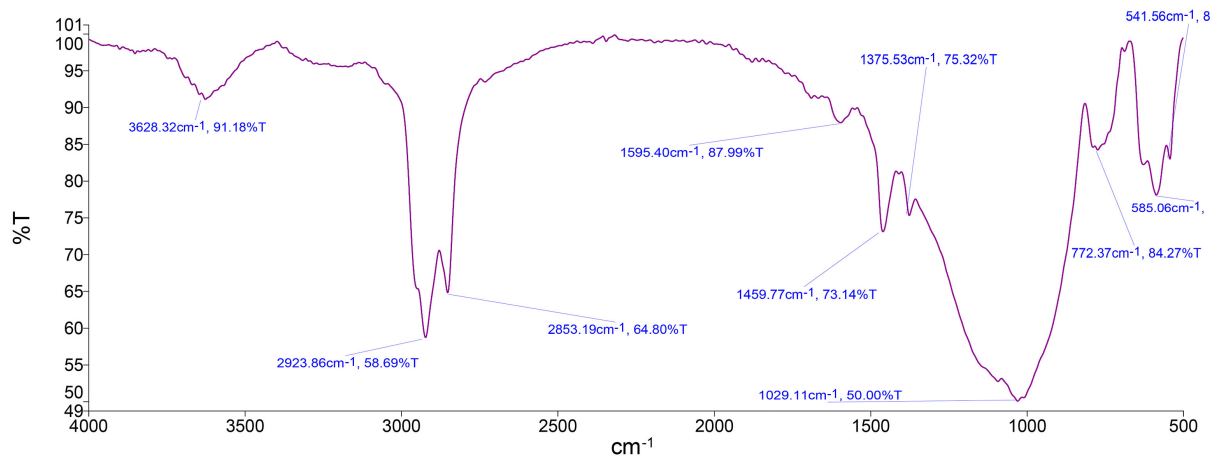


Figure 15. Spectrum of aged conventional asphalt mixtures.

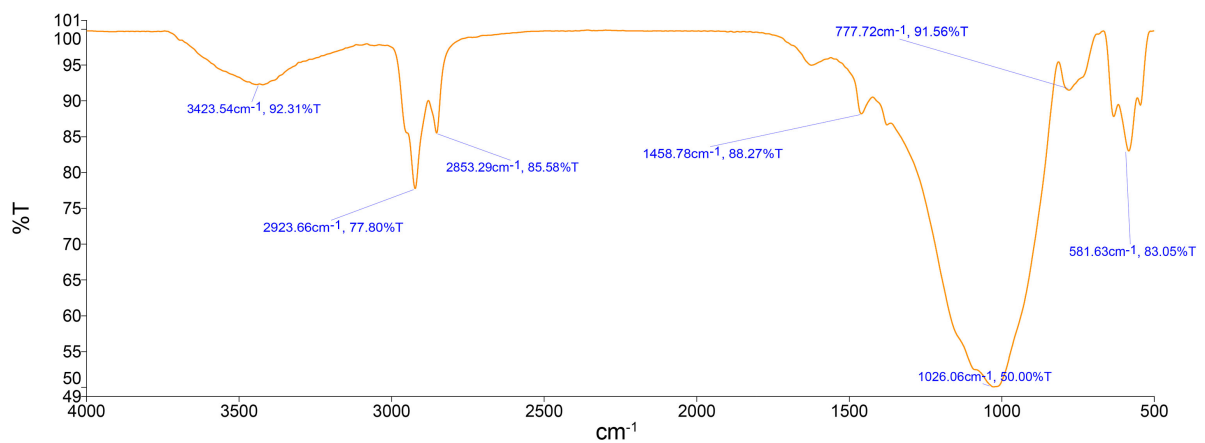


Figure 16. Spectrum of aged modified asphalt mixtures.

Figure 17 shows a comparative FTIR spectrum of aged, modified, and conventional asphalt mixtures. Both spectra exhibit oxidation bands, but the modified mixture retains hydrocarbon characteristics, suggesting that the allophane interaction helps mitigate asphalt deterioration. Likewise, the more pronounced peaks in the modified mixture, especially in the silicate region, indicate the presence of allophane and its significant contribution to aging resistance.

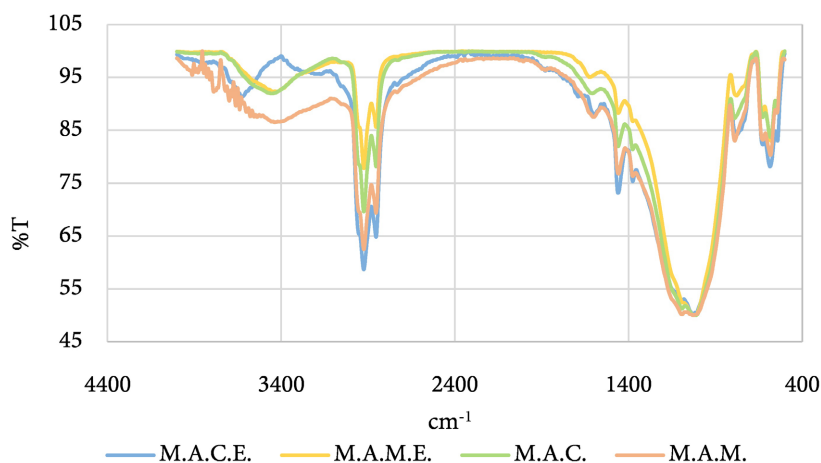


Figure 17. Spectrum of aged conventional and modified asphalt mixtures.

Table 9. Functional groups of asphalt mixture spectra.

| | Enlace/Grupo Funcional, IR [cm ⁻¹] | | | | | | |
|---|--|-----------------|-------------------------------------|---------|---------|--------|--------|
| | O-H | C-H (Aliphatic) | CH ₂ and CH ₃ | Si-O-Si | Si-O-Al | Al-O | |
| Conventional Asphalt Mixtures (M.A.C.) | 3457.1 | 2932.63 | 2853.06 | 1459.04 | 1014.25 | 788.91 | 582.18 |
| Modified Asphalt Mixtures (M.A.M.) | 3436.19 | 2923.44 | 2853.29 | 1457.04 | 1026.55 | 788.43 | 582.5 |
| Aged Conventional Asphalt Mixtures (M.A.C.E.) | 3628.32 | 2923.86 | 2853.19 | 1459.77 | 1029.11 | 772.37 | 585.06 |
| Aged Modified Asphalt Mixtures (M.A.M.E.) | 3423.54 | 2923.66 | 2853.29 | 1458.78 | 1026.06 | 777.72 | 581.63 |

Note. The table denotes the functional groups according to the wavelength of the asphalt mixtures.

Based on the FTIR results, a plausible chemical interaction mechanism between allophane and asphalt can be proposed. Allophane is characterized by a high density of surface hydroxyl groups (–OH), as evidenced by the broad absorption band around 3450 cm⁻¹. These hydroxyl groups can establish hydrogen bonding interactions with the polar fractions of asphalt, particularly resins and asphaltenes, as well as with oxygenated functional groups formed during aging. In addition, the presence of Si-O-Si and Si-O-Al bands confirms the silicate framework of allophane, which contributes to the formation of a physicochemical interfacial network within the asphalt binder (**Table 9**).

This network restricts molecular mobility and enhances internal cohesion, leading to a stiffer and more stable binder matrix. The preservation of aliphatic C-H bands indicates that the fundamental hydrocarbon structure of asphalt remains unchanged, while the increased intensity and persistence of hydroxyl-related

bands in the modified mixtures—particularly after aging—suggest that allophane plays a protective role against oxidative degradation. Consequently, the interaction between hydroxyl-rich allophane surfaces and asphalt components improves adhesion, reinforces the binder structure, and contributes to enhanced aging resistance.

The observed behavior indicates that allophane functions not merely as a filler, but as an active nano-modifier that alters the physicochemical balance of the asphalt binder.

3.2.6. Thermogravimetric Analysis (TGA)

TGA enabled evaluation of the thermal stability of the materials and discussion of the influence of allophane on the thermal degradation of asphalt mixtures and their resistance to high temperatures. The TGA and dTGA curves are analyzed below (Jiménez, 2018). The TGA curve of allophane shows a constant mass loss until reaching approximately 700°C. This behavior indicates good thermal stability, suggesting that allophane can act as a stabilizer in the asphalt mixture, minimizing the thermal degradation of asphalt (**Figure 18**). Additionally, the porous structure of allophane allows it to retain water and other compounds, potentially improving asphalt's thermal resistance by preventing the volatilization of critical components.

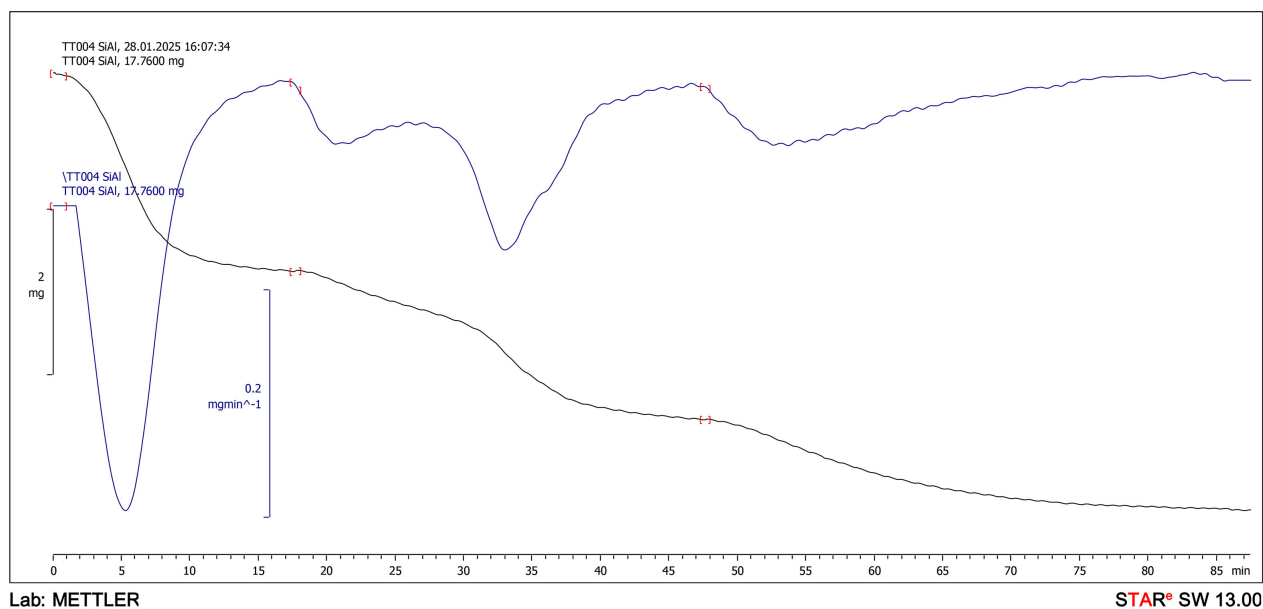


Figure 18. Allophane TGA and dTGA curve.

The TGA curve for the conventional mixture shows greater mass loss than that of allophane, suggesting that the mixture is more susceptible to thermal degradation. This can be translated into a lower resistance to high temperatures, which affects its durability (**Figure 19**). It also indicates that, under aging conditions, there is a greater breakdown of the asphalt components, implying that conventional asphalt could lose its effectiveness in retaining properties at high tempera-

tures.

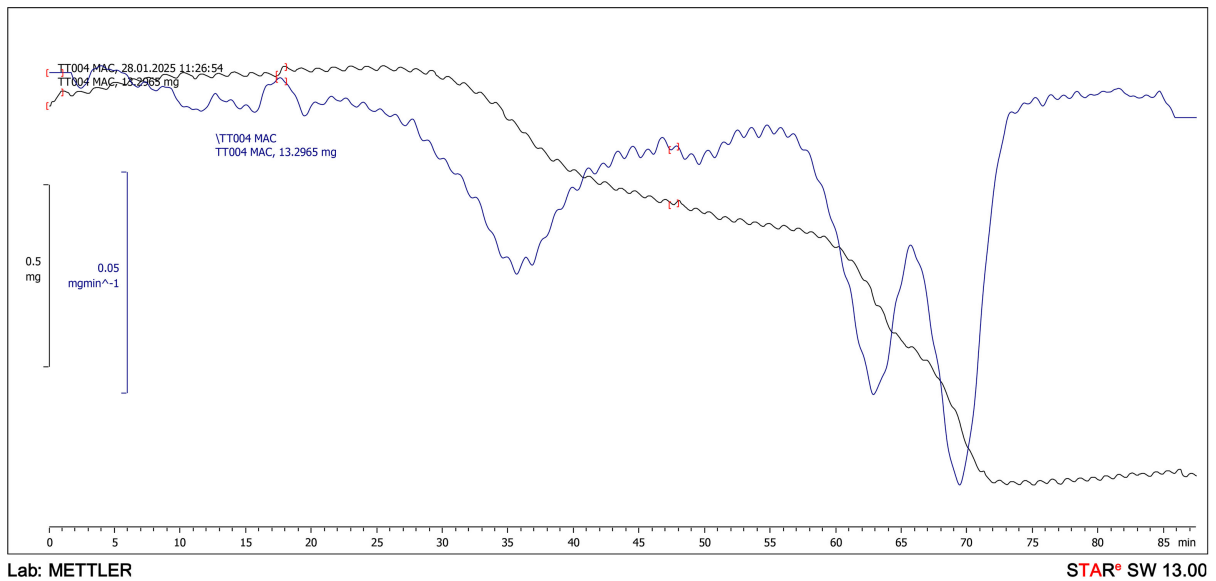


Figure 19. TGA and dTGA curves of non-aged conventional mixtures.

The TGA curve of the allophane-modified mixture shows a more controlled mass loss than the conventional mix, indicating that allophane improves the mixture's thermal stability (**Figure 20**). Modification with allophane appears to provide a synergistic effect, where the allophane structure helps maintain the integrity of the asphalt against heat degradation.

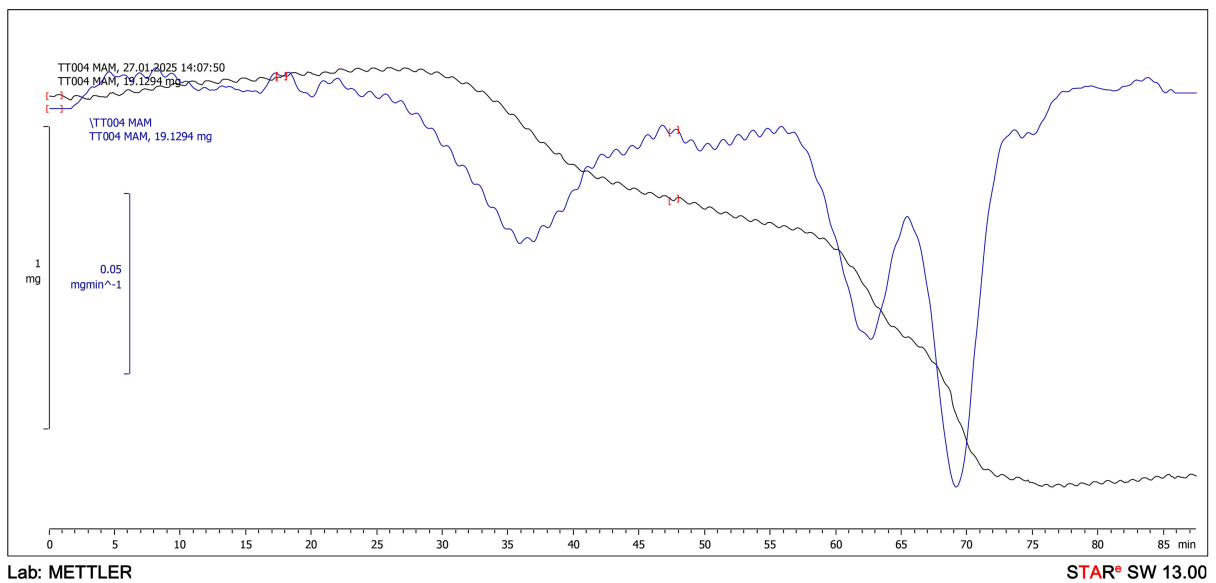


Figure 20. TGA and dTGA curves of modified, non-aged mixtures.

Aged conventional mixtures show a significant increase in mass loss compared to non-aged mixtures, indicating accelerated deterioration due to oxidation and volatilization of heat-sensitive components. This suggests that aging reduces the

asphalt's ability to withstand high temperatures, thus increasing the risk of cracking and structural failure (Figure 21).

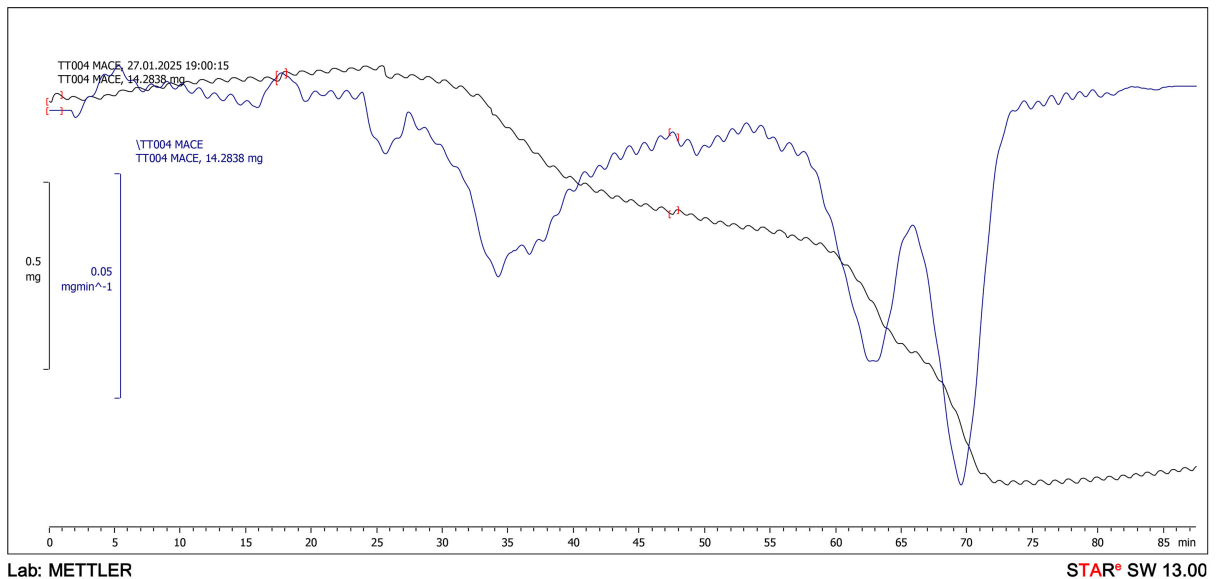


Figure 21. TGA and dTGA curves of aged conventional mixtures.

Finally, the aged allophane-modified mixture shows a more controlled mass loss compared to the aged conventional mixture, indicating that allophane helps to preserve the asphalt's properties over time. This suggests that, by incorporating allophane, the mixture not only improves its resistance to aging but also withstands higher temperatures without significant degradation (Figure 22).

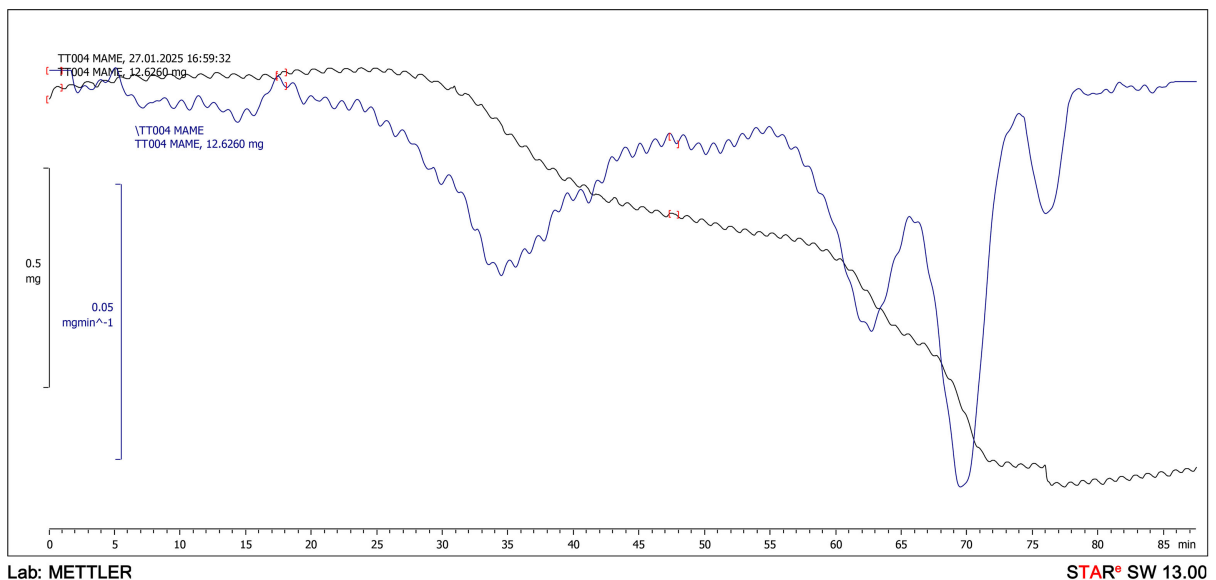


Figure 22. TGA and dTGA curves of aged, modified blends.

3.3. Summary of Integrative Results and Relevant Findings

The structural characterization of allophane confirmed its amorphous and nano-

metric nature (3.2 - 3.8 nm), attributes that explain its high surface reactivity and its ability to interact with matrices of different natures. This molecular behavior was reflected in the two systems studied: in mortars, where a reduction in capillary porosity led to a notable decrease in water absorption; and in asphalt mixtures, where allophane's interaction with the bituminous phase enhanced cohesion, wear resistance, and durability.

For mortars, the optimization model based on cubic spline interpolation showed that allophane can modify the material's response to capillary absorption in a non-linear manner. The experimental results showed a 23.7% reduction in absorption compared to the standard, with an additive concentration of 0.5%, a cement-to-sand ratio of 1:5, and a curing time of 28 days. In addition, the model identified optimal combinations by evaluating variables such as cement (sand ratio, curing time, and additive percentage). This confirms that allophane not only blocks permeability routes but also interacts with the cement matrix, stabilizing the microstructure and conferring greater uniformity in performance.

In asphalt mixtures, the incorporation of 0.25% allophane into 4.65% AC-20 asphalt improved physical-mechanical and rheological properties. An increase of $28.92 \pm 2\%$ in resistance was observed, accompanied by a significant improvement in thermal stability, as evidenced by lower mass loss and a higher degradation temperature in the TGA and DTGA curves. Additionally, the Fourier Transform Infrared Spectroscopy (FTIR) spectra showed that the functional groups in the modified asphalt binder were retained. This mechanism directly reduces oxidation, slows aging, and extends pavement service life. The chemical stability was also associated with a significant increase in surface wear resistance, as measured by the Cantabro test. Overall, the thermal stability and compatibility of the modified mixture meet the requirements set by national and international regulations, demonstrating the potential of allophane as a high-performance additive for durable asphalt pavements.

The analogies between both systems reveal a common principle: allophane, due to its surface area and porosity, functions as a microstructure-modulating agent, either by sealing capillaries in the mortar or by enhancing cohesion in the asphalt matrix. In both cases, its action results in decreased permeability, increased durability, and greater resistance to degradation, providing clear evidence of its multifunctional role as a nano-additive.

Nevertheless, each system has its own characteristics. In mortar, the main benefits are waterproofing and the ability to optimize dosage using predictive tools, enabling smart design of cementitious mixtures. In asphalt, the key advantage of bituminous modification is improved mechanical and thermal resistance, along with reduced binder aging, which are essential for extending pavement lifespan. Overall, the results demonstrate that allophane is a highly versatile nanotechnology additive capable of enhancing both mineral and bituminous matrices. This dual functionality emphasizes its scientific importance and enhances its potential to address structural challenges in the construction field.

4. Conclusions

4.1. Conclusions Regarding Mortar

The characterization of allophane using SEM, TEM electron microscopy, and BET analysis provided essential insights into its structural and morphological properties. The results confirm allophane's amorphous nature (**Figures 1-4**), characterized by the absence of a defined crystalline structure, irregular particle morphology, and rough surfaces. These features promote its interaction with the cementitious matrix, improving chemical and mechanical properties, especially impermeability. Similarly, the average particle size was determined to be between 3.2 and 3.8 nm.

The optimization model, developed using cubic spline interpolation and discrete data, is a robust tool for analyzing allophane-modified mortar behavior and aiding in mixture design decisions, allowing not only to identify the minimum necessary dosage to reduce water absorption but also to describe efficiency trends and generate alternative scenarios that complement the experimental evidence. For example, the model proposed a 1.53% additive dosage in a 1:3 cement-to-sand ratio at 28 days of curing (contrasting with 0% obtained experimentally), adjusting for an optimal dosage of 0.41% (**Table 4**) for a 1:5 cement-to-sand ratio and 28 days of curing (differentiating from the 0.5% experimental result); demonstrating the utility of integrating predictive modeling, which provides flexibility in evaluation and guarantees controlled absorption levels. The model is also designed to scale to larger datasets, allowing the incorporation of additional variables, such as compressive strength, workability, or durability, and to adapt to real field conditions.

4.2. Conclusions Regarding Asphalt

The results from the Indirect Tensile Strength (ITS)-Rigidity Modulus and Cantabro Wear Test converge to demonstrate that allophane acts as a polyvalent and highly effective modifier for asphalt mixtures. Allophane substantially improves the material's rigidity, tensile strength, and durability. On the one hand, it was found that allophane substantially improves the material's rigidity, tensile strength, and durability, an effect that is maintained across a wide range of temperatures and even enhanced with aging (**Table 8**), suggesting improved performance against cracking and deformation. On the other hand, evidence from the Cantabro test confirms that allophane significantly increases resistance to surface wear, which translates directly into a longer pavement lifespan and reduced maintenance costs.

The incorporation of allophane comprehensively improves the properties of asphalt mixtures. This study demonstrates that, when added at 0.25% to AC-20 asphalt, allophane not only significantly increases the mixture's strength by $28.92 \pm 2\%$, but also acts as a thermal stabilizer, as evidenced by TGA and DTGA curves showing less degradation at high temperatures (**Figures 18-22**). Likewise, the research confirms allophane's ability to mitigate the effects of aging. The FTIR spec-

tra (**Figure 17** and **Table 9**) indicate that allophane promotes greater retention of beneficial functional groups, which translates into better long-term performance. These improvements in strength, thermal stability, and durability over time position allophane-modified mixtures as a high-performance alternative capable of extending pavement lifespan. Allophane enhanced adhesion, asphalt absorption, cohesion, and overall compatibility within the mixture properties. The allophane-modified asphalt mixtures complied with both national and international technical standards, establishing them as a sustainable, high-performance alternative for constructing and maintaining flexible pavements (**Table 6**).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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